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THE STRUCTURE AND PROPERTIES OF MATERIALS WITH RENEWABLE SOURCES RAW MATERIALS

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ABSTRACT: The goal of the paper is present the preparation and evaluation of applications of polylactide fibres. The theoretical part of this work contains a knowledge review of development, structure, properties and application of polylactide fibres.
The paper presents:

- evaluation of physical and mechanical properties, structure parameters
- and thermal properties of polylactide fibres,
- evaluation of applications of polylactide fibres to the area of composites materials.

The biodegradability of lactic acid polymers showed no toxicological effect.

KEY WORDS: Polylactide polymers, Macromorfological structure, Biopolymers, Utilitarian properties.

1. INTRODUCTION

Many synthetic polymers are made of non-renewable resource - oil. Standard polymer systems are connected with a number of problems concerning negative impact on environment; several polymers are not recyclable. A new feedstock basis seems to be more suitable solution. It would replace oil and also provide polymers that are more acceptable for the environment.

Nowadays, the researchers are mainly interested in microbial polymer systems that are synthesized on the renewable and non-toxic product basis. The most significant process is now the polylactide production. Polylactides were interesting for the scientists as early as in the 19th century. The first researcher, who made polylactic acid in 1932, was Carothers. Since 1954 polylactides have been utilised in the medicine. Thanks to their biodegradation, biocompatibility and very good mechanical properties they have gradually found their use in various spheres. Industrially, polylactic acid is made of agricultural products containing starch (maize, potatoes, white beet, sugar cane, waste biomass). Polylactides are the only biopolymers produced in the industry area. Current world production of PLA is estimated to 250,000 tons and it is assumed that by the year 2008 it will increase to almost 400,000 tons [1].

1.1. Polylactide Fibre Properties

In connection with the mentioned facts, the application of polylactide fibres (PLA) in the technical textiles has become and is becoming even more interesting. The fibres made of polylactic acid are one of the most promising biodegradable fibres with natural and synthetic fibre properties. Polylactides are made of lactic acid. Lactic acid (α-hydroxypropion acid) is a simple natural organic acid that can be found in the bodies of animals, plants and microbes. It can be easily disintegrated in the nature without any harm to the environment. Lactic acid is capable of elf-polycondensation. It has asymmetric carbon and creates two optical isomers. It is made in the process of fermentation as well as L(+) lactic acid. Poly-L-lactic acid (PLLA) has desired crystallinity, while lactic acid copolymer L/D has lower crystallinity, or it is amorphous [1].

Table 1: Chemical structure of PLA [1]

Polymer	*Basic unit*	*Monomer*	*Note*
Polylactic acid (PLA)	$(\text{-O-CH-CO-})_n$ with CH_3 on CH	HO-CH-COOH with CH_3 on CH	Optical isomer L(+) and D(-)

The curve in Picture 1 indicates the dependence between PLA melting temperature and D- lactic acid isomer content. Including D(-) lactic acid to the PLA macromolecule pathway is also determined by polymer's crystallization ability together with its application characteristics [2].

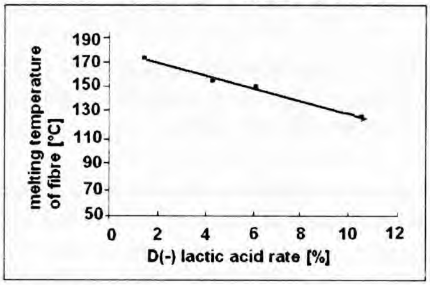


Fig. 1: Dependence between PLA melting temperature and D- isomer content [2]

1.2 PLLA and PLLA Fibres Chemical Properties

PLLA and PLLA fibres are always present in many dissolvents, including dry-cleaning reagents. They can be mixed with several dissolvents and can be dissolved in special dissolvents as shown in Table 2. PLLA fibres are very sensitive and easily degradable in water solution bases e.g. NaOH and KOH, while they are rather stable in acids, e.g. HCl. Molecular weight of these fibres is compared to PET and PA6. PLLA fibres can be stained with dispersed dye with sufficient resistance to light at the temperature of 98 - 110°C. That is why the PLLA fibres can be used also for clothes [1,2,3].

Table 2: PLLA and PLLA Fibres Chemical Properties [1]

Properties	*Characteristics*
Molecular weight	$Mw = 8\text{-}20.10^4$ $Mw/Mn = 2\text{-}3$
Melting temperature	320°C (Weight loss is 5% at DTA in N_2)
Resistance in dissolvents	1 Stable: methanol, isopropanol, hexane, petroleum-ether, water 2 Mixable: acetone, toluene, acetonitrile, methyl-ethylketone 3 Soluble: m-kerazol, dioxane, chloroform, methylene chloride
Resistance in basic dissolvent	Very sensitive, Rapidly degradable
Resistance in acid dissolvent	Rather stable, Degradation speed not fast
Capability of being stained	Stainable with disperse dye, Sufficient stability on light required

1.3 Physical and Mechanical Properties of PLLA and PLLA Fibres

In these days, the greatest attention is paid to physical modification based on macro-morphology and geometry changes of fibres. PLA polymer physical properties e.g. melting temperature and modules can be controlled through the copolymerisation method e.g. L- and D- acid or other comonomers copolymerisation.

PLLA fibres are firm and heat-resistant enough. Ductility and firmness can be regulated in the production process. It is easy to produce formed or flat fibres. Biodegradable fibres can be formed via improper twist. That is why the PLLA fibres can be utilised in textiles designed for clothes, soft furnishings, technical textiles and medical implants [1, 2, 3].

Table 3: PLLA Fibres Physical-Mechanical Properties [1]

Properties	PLLA
Density (g/cm^3)	1.27
Melting temperature (°C)	175
Crystallisation temperature (°C)	103
Glass transition temperature (°C)	58
Residual humidity (%)*	0.6
Combustion heat (kJ/kg)	19,000
Breaking strain (cN/dtex) (GPa)	4.0-5.5 0.40-0.55
Ductility (%)	20-35
Young's module (cN/dtex) (GPa)	60-70 6.0-7.0
Shrinkage in boiling water (%)	8-15

*Relative humidity 65%, t=25°C

Residual humidity is rather low. Thanks to above mentioned characteristics the clothes made of these fibres are cushy, fine and dry. Low break index ensures that the clothes are smooth with silk gloss. Melting temperature at 175°C is the highest from the group of other biodegradable polymers but always requires special attention during ironing. Combustion heat is lower than the combustion heat of other synthetic polymers [1,3].

1.4 PLA Production

The production includes water removal in milder environment without any dissolvent. The result of the process is cyclic dimer - lactide. Polymerisation with dimer ring-opening is finished while applying heat. Constant controlling of lactide clearness enables to produce a wide range of molecular weights. Lactic acid exists in two optical active forms [2].

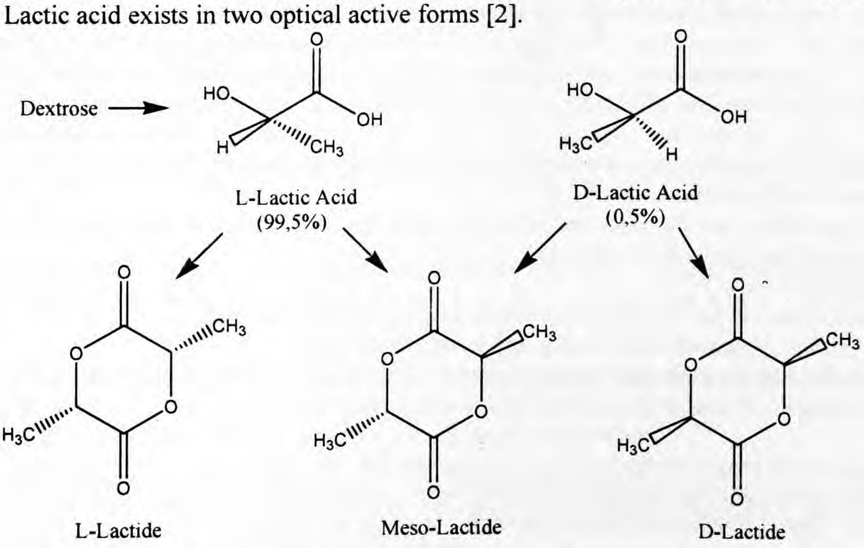


Fig. 2: Lactide intermediate products

Each phase of the process from maize to various products is shown in Picture 3 [4].

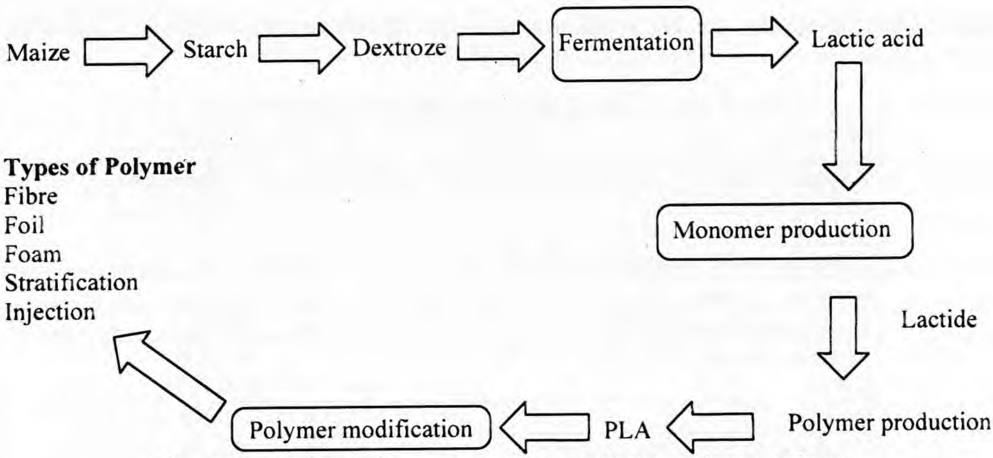


Fig. 3: Each phase of the process from maize to various products

PLA is made of lactic acid that is prepared in the process of corn starch fermentation (Picture 3). The fibre can be composted or disintegrated in soil to carbon dioxide and water through micro organism activity after use. In both cases it can be transformed to starch again through photosynthesis occurring in plants. PLA fibre is recyclable in natural environment without any harm to it [1].

Polylactide properties can be compared to standard thermoplastic or fibrous material. It has been used successfully in medicine and for pharmaceutical purposes. However, PLA attracted more attention for its metamorphoses, i.e. biodegradability and the fact that it is made of renewable resources [1].

1.5 PLLA and PLLA Fibres Biodegradability

Standard characteristic of microbial polymers (as well as polylactides as they also belong to this group) is their biodegradability. Biodegradable polymer can be disintegrated to low molecular substances in certain environments through micro organism activity [1,4].

In nature, PLLA proves rather low degree of degradation in comparison to other biodegradable polymers as polybutenesuccinate, poly-3-hydroxybuthyrat, modified starch, polykaprolakton. The level of degradation can be affected by PLLA modification. The process of degradation can be streamed by adding several hydrophilic components to the polymer or by decreasing crystallinity. That is why there are several processes how to produce different types of polymers with different level of degradation or different durability [1,2].

In dependence on the final usage of the fibre the PLLA fibre biodegradability was tested using several methods mentioned below [1]:

- Digging in soil
- Modification in river water and sea water using immerse method
- Activation of sewage water using impregnation method
- Modification in domestic composting device using standard composting method (CEN standard)

The fibre in soil proves rather low level of degradation. In 1 or 2 years, its firmness has gradually decreased and the weight loss has started to delay after certain period of time. This process is different in active mud. The disintegration level of the fibre was higher because of bacteria and micro organism activity. The fibre lost its firmness in 3 or 4 months and its weight approximately in 1 year. We can compare it to PET and PA fibres that were not disintegrated during this process; their original form and physical properties have remained unchanged. Cellulose-base fibres made of e.g. cotton, or raw silk, degrade faster than fibre made of PLLA [1,3].

2. EXPERIMENTAL PART

The aim of the experimental part of this work is to evaluate basic physical and mechanical properties of tested samples - polylactide fibres - in a traditional laboratory environment. The evaluation of basic structural parameters, using Light Microscopy, Scanning Electron Microscopy and the evaluation of thermal properties of polylactide fibres.

2.1 PLA Fibres Evaluation Results

Tested samples:

- PLA 1- hollow shear fibre (manufacturer: Cargill Dow LLC)
- PLA 2 - shear fibre with circular section (manufacturer: Toray Industries, Inc.)
- PLA 3 - infinite fibre with circular section (manufacturer: Toray Industries, Inc.)

2.1.1 Evaluation Results of Basic Physical and Mechanical Properties of PLA Fibres

Mechanical properties of fibres are dependent on conditions of their preparation as these conditions determine the structure development. Although in some applications the firmness is not so important, they must provide good level of processing using appropriate technologies and use property of a sample. Table 4 lists measured basic physical and mechanical parameters of tested samples - PLA fibres.

Table 4: Specified basic physical and mechanical property values of samples - PLA fibres.

Sample	Unit softness (dtex)	Firmness (cN/dtex)	Ductility (%)
PLA 1	8.03	1.03	39.28
PLA 2	1.85	2.21	50.90
PLA 3	2.32	3.63	31.0

2.1.2 Evaluation Results of Basic PLA Structural Parameters

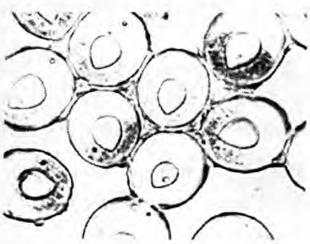


Fig. 4: Lateral section of PLA 1 sample with 740x zoom

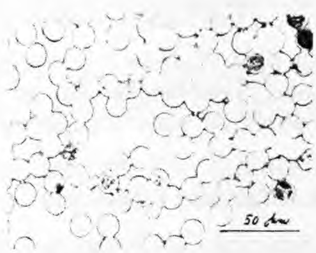


Fig. 5: Lateral section of PLA 2 sample

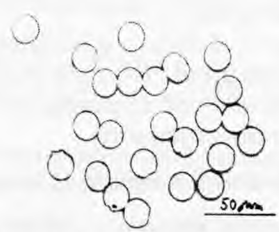
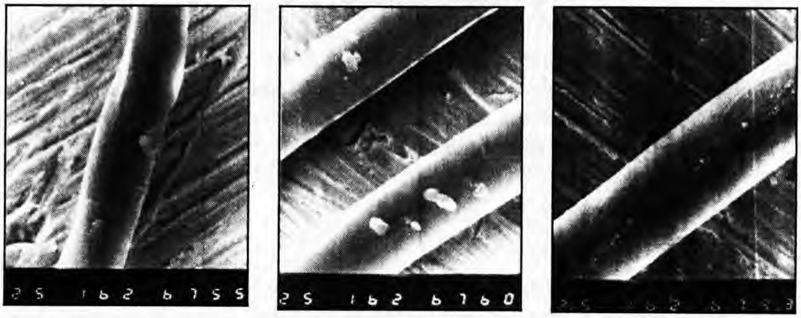


Fig. 6: Lateral section of PLA 3 sample

From the pictures, it is obvious that PLA 1 sample is a hollow shear fibre with circular section and smooth surface. PLA 2 and PLA 3 samples have circular section as well, but in comparison to PLA 1 sample they are not hollow; i.e. they are standard textile fibres.

Electron Microscopic Image (REM) of PLA fibre surface structure is shown in Picture 7. We can see oligomers on the fibre surface clearly; there is a significant fibrillar structure under the surface that builds the basic morphological unit of oriented fibre.



PLA 1 Sample PLA 2 Sample PLA 3 Sample

Fig. 7: REM images of PLA fibre surface

Fig. 8: REM images - internal morphological structure of PLA 3 fibre, using. Sample Peeling Preparation Technique

During the optical birefringence determination process using the Compensatory method following optical birefringence values have been measured: PLA.2 sample = $26{,}41.10^3$ and PLA 3 sample = $25{,}1.10^3$. These values are mentioned for comparison of the optical birefringence of the two samples. The optical birefringence is a value that represents the level of anisotropy, or overall orientation of polymer system.

Speed of sound was measured only for the infinite fibre and the measured value is $2{,}52.10^3$ ($km.s^{-1}$). The length of PLA 1 and PLA 2 shear fibres samples was not sufficient for this test. With the use of speed of sound measuring, we can determine some supramolecular structure parameters, especially average fibre orientation.

2.1.3 Evaluation Results of Basic PLA Thermal Properties

Thermal methods - Differential Scanning Calorimetry and Thermogravimetry - are used in the study of physical, chemical and physical-chemical changes of polymers and fibres in dependence on temperature. Polymer thermostability has its significance in the process of fibres or polymer products preparation as well as for ensuring good utility weight.

The result of Differential Scanning Calorimetry evaluation is presented in DSC curves that characterise the melting process and from which the melting temperature Tm (°C) was subtracted, and melting enthalpy of sample ΔHm (kJ/kg) shown in Table 5. On the basis of sample melting enthalpy and theoretic melting enthalpy of total crystallic areas (ΔH = 93 kJ/kg), the crystallic ratio Kp (%) was calculated for the PLA samples, also shown in Table 5. The crystallic ratio shows clearly that the highest value was measured for infinite fibres, i.e. PLA 3 sample.

Table 5: Measured melting temperature of PLA fibres

Sample	ΔHm (kJ/kg)	**Tm (°C)**	**Kp (%)**
PLA 1	44.5 ± 2.2	164.5 ± 1	47.9
PLA 2	47.5 ± 2.4	163.0 ± 1	51.1
PLA 3	49.1 ± 2.5	159.2 ± 1	52.8

Shear fibres PLA 1 and PLA 2 were analysed using Thermogravimetry (TG) in the dynamic test at temperatures up to 350°C and isothermal test at temperatures up to 230°C.

Measured weight losses at isothermal temperature up to 230°C prove that both samples have almost identical low weight losses. The samples are stable at this temperature and solid state after melting is white; there is no change of colour. The dependence between weight change of PLA 1 and PLA 2 samples and stop period is shown in Picture 9.

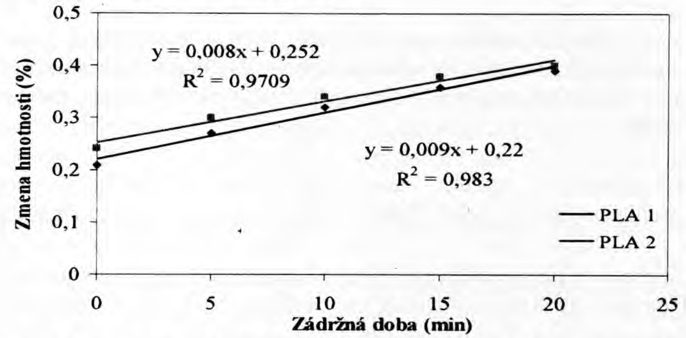


Fig. 9: The dependence between weight change of PLA 1 and PLA 2 samples and stop period (TG measuring at 230°C)

3 CONCLUSION

The aim of this work was to evaluate the polylactide fibres structure and properties.
On the basis of the measured values we can formulate following conclusions:

- Upon the results of physical-mechanical and structural properties evaluation we can presume that structural parameters and subsequently physical-mechanical properties change in the production process.
- Upon the results of weight loss evaluation in the process of PLA fibres thermal chaining we can assume that polymers have good thermostability at 230°C, which is sufficient for PLA polymer melt-spinning.
- DSC results prove good crystallisation based on polylactide fibres preparation conditions and most of all molecular structure concerning high content of L-form in lactic acid.

PLA fibres properties described here maintain the production of various applicable fibre forms abroad and also on the domestic market. As polylactides belong to a new fibre type, availability of resources, causing no harm to environment, and expected primary costs indicate that polylactides are the fibres of the third millennium.

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